PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 25 August 2000 (25.08.00)	
International application No. PCT/GB00/00402	**Applicant's or agent's file reference** 4576F/JAK
International filing date (day/month/year) 10 February 2000 (10.02.00)	**Priority date** (day/month/year) 12 February 1999 (12.02.99)
Applicant SIDDLE, John, Robert	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

10 July 2000 (10.07.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Juan Cruz
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C03C 17/36, 17/09, C23C 14/54 — A1

(11) International Publication Number: **WO 00/47530**

(43) International Publication Date: 17 August 2000 (17.08.00)

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(30) Priority Data:
9903056.1 12 February 1999 (12.02.99) GB

(71) Applicant *(for all designated States except US)*: PILKINGTON PLC [GB/GB]; Prescot Road, St. Helens, Merseyside WA10 3TT (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: SIDDLE, John, Robert [GB/GB]; 25 Knowsley Road, Southport, Merseyside PR9 0HW (GB).

(74) Agents: HALLIWELL, Anthony, Charles et al.; Group Intellectual Property Dept., Pilkington European Technical Centre, Pilkington plc, Hall Lane, Lathom, Ormskirk, Lancashire L40 5UF (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: IMPROVEMENTS IN COATING GLASS

(57) Abstract

A process for the production of a coated substrate, preferably glass, comprising depositing a reflective metal, especially a silver, layer by a low pressure deposition process performed in a coating atmosphere that contains a gaseous oxygen scavenger. The presence of the gaseous oxygen scavenger alleviates oxidation of the silver layer by any oxygen gas present in the coating atmosphere. The gaseous oxygen scavenger may be a hydrocarbon and is preferably methane. The coating process is preferably sputtering.

09/890413

PATENT COOPERATION TREATY

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REC'D 29 JUN 2001
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
4576F/JAK		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB00/00402	10/02/2000	12/02/1999
International Patent Classification (IPC) or national classification and IPC C03C17/36		
Applicant PILKINGTON PLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☒ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
10/07/2000	27.06.2001
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Van Bommel, L Telephone No. +31 70 340 2747

Form PCT/IPEA/409 (cover sheet) (January 1994)

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/00402

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-7 as originally filed

Claims, No.:

1-23 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-20
	No:	Claims	21-23
Inventive step (IS)	Yes:	Claims	1-20
	No:	Claims	21-23
Industrial applicability (IA)	Yes:	Claims	1-23
	No:	Claims	

2. Citations and explanations
see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Subject-matter

Claims 1 - 20 of the application define a low pressure deposition process for coating a substrate with a reflective metal layer performed in a coating atmosphere that contains an oxygen scavenger. Independent process claim further defines that hydrogen as an oxygen scavenger is excluded when a multilayer is deposited comprising a bismuth oxide layer. Independent process claim 19 further defines an evacuation step and defines the evacuation and coating pressures.
Furthermore, claims 21 - 23 define coated products and the use of an oxygen scavenger.

2. Novelty

US-A-5 837 361 describes a process for coating glass with a multilayer stack comprising oxide layers and a silver layer. According to Example 1 the sputtering of the metallic silver layer takes place in an atmosphere containing hydrogen. since bismuth oxide is one of the layers in the examples, the teaching of US-A-5 837 361 is excluded from claim 1 of the application. US-A-5 837 361 is silent on the evacuation step and pressures defined in claim 19.
Therefore, the processes of claims 1 - 20 are new w.r.t. US-A-5 837 361.

However, claims 21 and 22 define products produced by a process according to one of the process claims ("product-by-process claims").
It is considered that the products obtained according to D1 are not different from the products defined in claims 21 and 22, since the hydrogen as used in D1 acts as an oxygen scavenger, and it is not apparent (e.g. from the present description) that oxygen scavengers different from hydrogen have an effect on the coated product that makes the coated products distinguishable from the ones obtained in D1.

Furthermore, the use of claim 23 does not seem to be new with respect to D1, since the hydrogen as used in D1 **acts as an oxygen scavenger** in the same process as defined in claim 23, although it is not mentioned in D1 as having this effect.

Re It m VI

Certain documents cited

Certain published documents (Rule 70.10)

Application No Patent No	Publication date *(day/month/year)*	Filing date *(day/month/year)*	Priority date *(valid claim)* *(day/month/year)*
EP-A-983 973	08.03.2000	02.08.1999	04.08.1998

In this document the use an oxygen scavenger in the sputtering atmosphere is mentioned. Although the oxygen scavenger is only used during the deposition of the metal oxide layer over the silver layer, this interferes with the embodiment of the invention described on page 3, paragraph 6, according to which the oxygen scavenger leaks from second coating atmosphere into the first. The fact that this might happen in state of the art processes (as the one disclosed in EP-A-983 973) is confirmed by GB-A-2 129 831, page 4, lines 60 - 63.

P NT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
4576F/JAK		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB 00/ 00402	10/02/2000	12/02/1999
Applicant		
PILKINGTON PLC et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PC[redacted]B 00/00402

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/36 C03C17/09 C23C14/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 983 973 A (FLACHGLAS AG ;PILKINGTON BROTHERS PLC (GB)) 8 March 2000 (2000-03-08) *cited in view of the embodiment of the invention described on page 3, par. 6* the whole document	1-7, 11-18, 20-23
X	US 5 837 361 A (HEINZ DECEASED BERNHARD ET AL) 17 November 1998 (1998-11-17) cited in the application claims; example 1	21-23
A		1-20
A	GB 2 129 831 A (PILKINGTON BROTHERS PLC) 23 May 1984 (1984-05-23) cited in the application page 1, line 40 -page 2, line 10 page 4, line 60 - line 63	1-23

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 April 2000	27/04/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Bommel, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/[redacted] 00/00402

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0983973 A	08-03-2000	NONE	
US 5837361 A	17-11-1998	DE 19541937 C	28-11-1996
		EP 0773197 A	14-05-1997
		JP 9174751 A	08-07-1997
GB 2129831 A	23-05-1984	AT 31525 T	15-01-1988
		AU 554729 B	28-08-1986
		AU 1928583 A	12-12-1985
		CA 1203197 A	15-04-1986
		DK 431483 A,B,	22-03-1984
		EP 0104870 A	04-04-1984
		FI 833385 A,B	22-03-1984
		JP 5024987 B	09-04-1993
		JP 59076534 A	01-05-1984
		MX 172033 B	29-11-1993
		NO 833335 A,B,	22-03-1984
		US 4462883 A	31-07-1984
		ZA 8306920 A	24-04-1985

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C03C 17/36, 17/09, C23C 14/54

A1

(11) International Publicati n Number: WO 00/47530

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(30) Priority Data:
9903056.1 12 February 1999 (12.02.99) GB

(71) Applicant *(for all designated States except US)*: PILKINGTON PLC [GB/GB]; Prescot Road, St. Helens, Merseyside WA10 3TT (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: SIDDLE, John, Robert [GB/GB]; 25 Knowsley Road, Southport, Merseyside PR9 0HW (GB).

(74) Agents: HALLIWELL, Anthony, Charles et al.; Group Intellectual Property Dept., Pilkington European Technical Centre, Pilkington plc, Hall Lane, Lathom, Ormskirk, Lancashire L40 5UF (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: IMPROVEMENTS IN COATING GLASS

(57) Abstract

A process for the production of a coated substrate, preferably glass, comprising depositing a reflective metal, especially a silver, layer by a low pressure deposition process performed in a coating atmosphere that contains a gaseous oxygen scavenger. The presence of the gaseous oxygen scavenger alleviates oxidation of the silver layer by any oxygen gas present in the coating atmosphere. The gaseous oxygen scavenger may be a hydrocarbon and is preferably methane. The coating process is preferably sputtering.

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Improvements in Coating Glass

This invention relates to a process for the production of a coated substrate and, in particular, it relates to a process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process.

Substrates coated with a reflective metal layer, typically silver 5 nm to 30 nm thick, may be produced with low emissivity and a high visible light transmission i.e. reflecting a high proportion of infra-red radiation incident upon them but allowing visible radiation to pass through. For optimum light transmission the silver layers are sandwiched between anti-reflection layers usually of metal oxide. The use of such coatings on window glass leads to a reduction in heat loss. Substrates having such coatings are described, for example, in UK patent specification GB 2 129 831.

Coatings having multiple (usually two) silver layers, each silver layer being sandwiched between anti-reflection layers, may also be produced. Coatings with multiple silver layers have both low emissivity, and with appropriate layer thicknesses, a low transmission of solar heat.

Coatings with silver layers are produced by deposition processes in a coating atmosphere at low pressure, especially by sequential deposition of a metal oxide anti-reflection layer, a silver layer, and a metal oxide anti-reflection layer. The metal oxide layers are usually deposited by reactive sputtering in a coating atmosphere containing oxygen and an inert gas (usually argon). Silver and other reflective metal layers are deposited by sputtering in an inert gas (usually argon). In US patent specification 5,837,361 a process for the production of a coating having layers of bismuth oxide (Bi_2O_3), zinc oxide, silver, nichrome, tin oxide and bismuth oxide is described, the metal oxide layers being reactively sputtered in an argon atmosphere containing oxygen and the silver layer being sputtered in an argon atmosphere with the addition of 5% by volume hydrogen.

In commercial production of sputtered coatings, sputtering of each layer usually proceeds in a sputtering chamber that has been initially evacuated to high vacuum (usually of about 10^{-6} mbar) and then raised to an operating pressure of around 10^{-3} mbar by flowing the gases making up the coating atmosphere into the chamber. The operating pressure is low so that the path length of the coating species sputtered from the target is high enough to reduce scattering and thereby maintain the efficiency of the coating process. Deposition of coatings may be performed in a single chamber having a readily changeable atmosphere or multiple,

serially connected deposition chambers each containing the desired atmosphere. In the multiple chamber case, the substrate is moved sequentially between the chambers, which are separated by gas-tight slit valves to alleviate leakage of the coating atmosphere between chambers. It is particularly important to alleviate leakage of oxygen from the metal oxide deposition chambers to the silver deposition chambers because the reflective metal layer oxidises or degrades if deposited in a coating atmosphere containing oxygen. To reduce leakage further there are usually additional chambers, positioned between the deposition chambers, which are pumped at high rates so that oxygen in the coating atmospheres used for sputtering metal oxide layers is removed before it can leak into the silver deposition chamber.

The need for high pumping rates in the deposition chambers and in the additional chambers requires expensively high pumping capacity, slows production rates considerably and leakage can still occur. Particular problems arise where the substrate to be coated is curved. In order to accommodate the greater cross-section of curved substrates, high clearance slit valves are required with an increased likelihood of leakage and in consequence a need for even higher pumping rates.

We have discovered that a low pressure deposition process for depositing a reflective metal layer can tolerate the presence of oxygen if a gaseous oxygen scavenger is present in the coating atmosphere.

The present invention accordingly provides a process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere, characterised in that the coating atmosphere contains a gaseous oxygen scavenger, wherein when the reflective metal layer is deposited as a layer in a multilayer coating which also contains a bismuth oxide layer said gaseous oxygen scavenger is not hydrogen.

In a preferred aspect, the present invention provides a process for the production of a coated substrate, characterised in that the coating atmosphere contains a gaseous oxygen scavenger other than hydrogen.

Oxygen can be present at a level that is too low to conveniently measure but nevertheless is high enough to oxidise or degrade the reflective metal layer. Thus, the coating atmosphere may contain the oxygen scavenger as a preventative measure, even if the deposition process is performed in a coating atmosphere that contains no measurable amount of oxygen.

Usually, the deposition process is performed in a coating atmosphere that contains oxygen (i.e. that contains a measurable amount of oxygen). The presence of oxygen in the coating atmosphere may arise by leakage from a deposition chamber containing a second coating atmosphere that contains oxygen or from outside (e.g. from the air).

The gaseous oxygen scavenger may be any substance capable of combining chemically with oxygen under the conditions of the low pressure deposition process. Such combination may take place in the gas phase or on the surface of the substrate.

Preferably each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom or more preferably with more than one molecule of oxygen. This is advantageous because then only a small amount of oxygen scavenger need be added to the first coating atmosphere. Adding a large amount of oxygen scavenger to the atmosphere may increase the pressure and therefore reduce the efficiency of deposition. Preferably the gaseous oxygen scavenger has a relatively high vapour pressure at room temperature.

It is advantageous if the gaseous oxygen scavenger is such that the products of its interaction with the surface of the reflective metal layer or of its combination with oxygen are themselves gaseous because the likelihood of solids contamination of the reflective metal layer is thereby reduced. A preferred oxygen scavenger is a hydrocarbon (for example an alkane, alkene, or alkyne), more preferably a C_1 to C_4 hydrocarbon (for example ethane, ethylene, acetylene, propane or butane) and most preferably methane. Oxygen scavengers that are less preferred but may also be suitable include hydrogen carbon monoxide, nitric oxide and organic compounds, for example, methanol, ethanol or formaldehyde.

Preferably, the reflective metal layer is deposited in a coating atmosphere comprising a flowing gaseous mixture and wherein the gaseous oxygen scavenger is introduced into the coating atmosphere by incorporation in the flowing gaseous mixture.

The gaseous oxygen scavenger may also or alternatively be introduced into the coating atmosphere by incorporating it into a second coating atmosphere of e.g. a second deposition chamber so that at least some of it can leak from that second coating atmosphere into the first.

The amount of oxygen scavenger in the coating atmosphere should not be so great as to unacceptably increase the pressure, but should be sufficient to alleviate oxidation or degradation of the reflective metal layer. In practice, if the quality of the reflective metal coating deteriorates during deposition (the deterioration is determined, for example, by an increase in sheet resistance), the amount of oxygen scavenger in the coating atmosphere would be increased to reverse, alleviate or prevent the deterioration.

Thus, preferably, the coating atmosphere contains the gaseous oxygen scavenger in an amount that is sufficient to alleviate oxidation and/or degradation of the reflective metal layer.

Usually the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen, preferably that exceeds 30 mol% of the amount of oxygen, and more preferably that exceeds 50 mol%, of the amount of oxygen.

Preferably, the reflective metal layer is a silver layer, and preferably the reflective metal layer has a thickness in the range 5 to 30 nm, more preferably in the range 7 to 18 nm. At thicknesses lower than about 5 nm the reflective metal layer may be discontinuous (this results from the growth mechanism of a layer and may occur even on a flat substrate) and will then not possess the properties of the bulk metal resulting in poor infra red reflecting properties. Thicknesses higher than about 30 nm may cause the coated glass to have too high a visible light reflectivity.

It is known to estimate the infra red reflection of reflective metal layers by measuring the sheet resistance of the coating. A high sheet resistance indicates poor infra red reflecting properties (i.e. high emissivity), whereas a low sheet resistance indicates good infra red reflecting properties (i.e. low emissivity). Oxidation or oxygen induced degradation of a reflective metal layer increases the sheet resistance with consequently poorer infra red reflecting properties. The sheet resistance of a layer is defined as:

$$R_S = \rho / d$$

where ρ is the resistivity of the layer, and d is its physical thickness (see, for example, *Thin Film Technology*, R.W. Berry, P.M. Hall and M.T. Harris (D. Van Nostrand, 1968) pp 329-331). The units of sheet resistance are Ω / square.

In the present invention, preferably the sheet resistance of the reflective metal layer is below 12 Ω / square. It is advantageous if, in the process, the coating atmosphere contains a measurable amount of oxygen and the sheet resistance of the reflective metal layer deposited in a first coating atmosphere containing oxygen is below 12 Ω/square, preferably below about 8 Ω/square.

In a preferred embodiment, the process additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer. The metal oxide layer will usually be deposited from a coating atmosphere that contains oxygen. Usually, at least two metal oxide anti-reflection layers will be deposited so

that the reflective metal layer is sandwiched between metal oxide anti-reflection layers. When two or more reflective metal layers are deposited (e.g. to provide a coating with low solar heat transmission) each reflective metal layer will usually be sandwiched between metal oxide anti-reflection layers. Examples of metal oxides suitable for use as anti-reflection layers include: zinc oxide, tin oxide, silicon oxide, zirconium oxide, titanium oxide, niobium oxide, molybdenum oxide, tungsten oxide, silicon nitride, silicon oxynitride and silicon oxycarbide. Additional layers of metal oxide, metals (e.g. nichrome, inconel or titanium) or other materials may also be present in the multi-layer coating by, for example, being deposited between the metal oxide anti-reflection layers and the reflective metal layers and/or between the substrate and a metal oxide layer.

Low pressure deposition processes are performed in flowing gas at pressures of below about 10^{-1} mbar, or preferably lower and include such processes as sputtering, reactive sputtering, evaporation and other forms of physical vapour deposition. The preferred low pressure deposition process for depositing the reflective metal layer is sputtering.

In prior art processes, deposition of each layer usually proceeds in a sputtering chamber, which has been initially evacuated to about 10^{-6} mbar to ensure removal of air, especially oxygen. The pressure of the chamber is then raised to an operating pressure of approximately 10^{-3} mbar by injection of the gases making up the coating atmosphere (usually argon for sputtering of the reflective metal and a mixture of argon and oxygen for sputtering of metal oxides).

The present invention is of particular benefit because with a gaseous oxygen scavenger present in the coating atmosphere, the deposition process is better able to tolerate incomplete removal of air.

Thus, in one embodiment, the present invention additionally provides a low pressure process for the deposition of a reflective metal layer on a substrate, performed in a deposition chamber containing a coating atmosphere, comprising evacuating the deposition chamber to a low first pressure, introducing a coating gas into the deposition chamber thereby raising the pressure therein to a higher second pressure of about 10^{-3} mbar, and sputtering the reflective metal layer at the second pressure, characterised in that the first pressure is about 10^{-4} mbar and in that the coating atmosphere contains a gaseous oxygen scavenger.

This is advantageous because evacuating to a higher pressure is more easily, rapidly and cheaply achieved (particularly because a lower pumping capacity is required).

The substrate to be coated is preferably glass but may be, for example, a transparent plastics substrate. The substrate may be flat or curved.

Coated glass produced by a process according to the invention has uses in many areas of glass use including in multiple glazing units and in laminated glass. Thus, in a further aspect the present invention provides coated glass comprising a glass substrate and a multilayer coating deposited on a surface of the glass substrate, wherein said multilayer coating comprises, in sequence, a first metal oxide anti-reflection layer, a reflective metal layer and a second metal oxide anti-reflection layer, characterised in that the reflective metal layer is deposited by a low pressure deposition process performed in a coating atmosphere containing a gaseous oxygen scavenger other than hydrogen.

In a further embodiment, the present invention provides use of a gaseous oxygen scavenger to reduce oxidation or oxygen induced degradation of a reflective metal layer in a process for the production of a coated substrate, said process comprising depositing the reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere containing the oxygen scavenger.

The invention is illustrated by the following Examples in which silver reflective metal layers were deposited on glass substrates by sputtering in a coating atmosphere containing argon, oxygen to simulate oxygen leakage and methane as gaseous oxygen scavenger.

Examples 1-5

Layers of silver were deposited on soda-lime glass substrates (of dimension 20 x 20 cm, 20 x 10 cm or 20 x 40 cm) at room temperature and at a pressure of 2×10^{-3} mbar by DC magnetron sputtering using a silver target of 99.9% purity and a power density (over approximately 160 cm^2) of about 3.1 W/cm^2. The coating atmosphere consisted of argon, oxygen and methane. All gases were obtained from B.O.C. Ltd and were Zero grade.

The glass substrates were positioned vertically in a holder and advanced at a glass traversal speed of 10-35 cm/min through the sputtering zone with a coating aperture of dimension approximately 1 cm.

After coating, the thickness of the silver layer was measured by computer fitting the optical transmission and reflection spectra of the coated glass, the spectra having been determined using a Hitachi U400 spectrophotometer.

The sheet resistance (in ohm/square) of the silver coatings was determined by a non-contact conductance monitor (Delcon Instruments 717 Conductance monitor).

Table 1 describes, for Examples 1-5, the flow rates of the gases in the coating atmosphere (in standard cm^3 per minute), the glass traversal speed, the thickness of the silver layer as determined and the sheet resistance of the coated glass.

Comparative Examples A and B

Comparative Example A was conducted under the same conditions as Example 1 except that no oxygen and no methane were present in the coating atmosphere.

Comparative Example B was also conducted under the same conditions as Example 1 except that no methane was present in the coating atmosphere.

Table 2 describes, for Comparative Examples A and B, the flow rates of the gases in the coating atmosphere, (in standard cm^3/min), the glass traversal speed, the thickness of the silver layer and the sheet resistance of the coated glass.

Table 1

Example	Flow rates of gases (standard cm^3/min)			Glass traversal speed (cm/min)	Thickness of silver layer (nm)	Sheet resistance (Ω/square)
	Ar	O_2	CH_4			
1	22	4	6	35	7.3	8.1
2	22	4	6	25	11.6	5.3
3	22	4	0.6	35	9.2	12.0
4	22	40	20	20	8.7	11.9
5	22	40	30	10	15	3.8

Table 2

Comparative Example	Flow rates of gases (standard cm^3/min)			Glass traversal speed (cm/min)	Thickness of silver layer (nm)	Sheet resistance (Ω/square)
	Ar	O_2	CH_4			
A	22	-	-	35	9.2	5.0
B	22	4	-	35	9.2	12.5

Claims

1. A process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere, characterised in that the coating atmosphere contains a gaseous oxygen scavenger, wherein when the reflective metal layer is deposited as a layer in a multilayer coating which also contains a bismuth oxide layer, said gaseous oxygen scavenger is not hydrogen

2. A process as claimed in claim 1 wherein the process is characterised in that the coating atmosphere contains a gaseous oxygen scavenger other than hydrogen.

3. A process as claimed in claim 1 or claim 2 wherein each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom of oxygen.

4. A process as claimed in any one of the preceding claims wherein the gaseous oxygen scavenger is a hydrocarbon.

5. A process as claimed in claim 4 wherein the gaseous oxygen scavenger is a C_1 to C_4 hydrocarbon.

6. A process as claimed in claim 5 wherein the gaseous oxygen scavenger is methane.

7. A process as claimed in any one of the preceding claims wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that is sufficient to alleviate oxidation and/or degradation of the reflective metal layer.

8. A process as claimed in one of the preceding claims wherein the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen.

9. A process as claimed in claim 8 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that exceeds 30 mol% of the amount of oxygen.

10. A process as claimed in claim 9 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that exceeds 50 mol% of the amount of oxygen.

11. A process as claimed in any one of the preceding claims wherein the reflective metal layer is a silver layer.

12. A process as claimed in any one of the preceding claims wherein the reflective metal layer has a thickness in the range 5 to 30 nm.

13. A process as claimed in claim 12 wherein the reflective metal layer has a thickness in the range 7 to 18 nm.

14. A process as claimed in any one of the preceding claims wherein the sheet resistance of the reflective metal layer is below 12 Ω / square.

15. A process as claimed in any one of the preceding claims wherein the coating atmosphere contains a measurable amount of oxygen and the sheet resistance of the reflective metal layer deposited in the coating atmosphere is below 12 Ω / square.

16. A process as claimed in claim 15 wherein the sheet resistance of the reflective metal layer deposited in the coating atmosphere is below 8 Ω / square.

17. A process as claimed in the preceding claims wherein the low pressure deposition process for depositing the reflective metal layer is sputtering.

18. A process for production of a coated substrate as claimed in any one of the preceding claims that additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer.

19. A low pressure process for the deposition of a reflective metal layer on a substrate, performed in a deposition chamber containing a coating atmosphere, comprising evacuating the deposition chamber to a low first pressure, introducing a coating gas into the deposition chamber thereby raising the pressure therein to a higher second pressure

of about 10^{-3} mbar, and sputtering the reflective metal layer at the second pressure, characterised in that the first pressure is about 10^{-4} mbar and in that the coating atmosphere contains a gaseous oxygen scavenger.

20. A process as claimed in any one of the preceding claims wherein the substrate is curved.

21. Coated glass produced by a process as claimed in any one of the preceding claims.

22. Coated glass comprising a glass substrate and a multilayer coating deposited on a surface of the glass substrate, wherein said multilayer coating comprises, in sequence, a first metal oxide anti-reflection layer, a reflective metal layer and a second metal oxide anti-reflection layer, characterised in that the reflective metal layer is deposited by a low pressure deposition process performed in a coating atmosphere containing a gaseous oxygen scavenger other than hydrogen.

23. Use of a gaseous oxygen scavenger to reduce oxidation or oxygen induced degradation of a reflective metal layer in a process for the production of a coated substrate, said process comprising depositing the reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere containing the oxygen scavenger.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 00/00402

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/36 C03C17/09 C23C14/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 983 973 A (FLACHGLAS AG ;PILKINGTON BROTHERS PLC (GB)) 8 March 2000 (2000-03-08) *cited in view of the embodiment of the invention described on page 3, par. 6* the whole document	1-7, 11-18, 20-23
X	US 5 837 361 A (HEINZ DECEASED BERNHARD ET AL) 17 November 1998 (1998-11-17) cited in the application claims; example 1	21-23
A		1-20
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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